

MARKED-UP VERSION OF SUBSTITUTE SPECIFICATION**ELECTRON SPECTROSCOPE WITH EMISSION INDUCED BY A
MONOCHROMATIC ELECTRON BEAM**Field of the Invention

[0001] The present invention relates in general to spectroscopy, and more in particular, to ~~systems of a~~ spectroscopic ~~investigations based on~~ system the ~~analysis of~~ analyzes the energy distribution of electrons emitted by a sample suitably excited by irradiation.

Background of the Invention

[0002] Electron spectroscopy analysis is ~~one of the~~ most ~~an~~ important techniques ~~of investigation of~~ for investigating solid materials.

Basically, there are two types of spectroscopy systems. Each ~~with~~ system has peculiar characteristics and ~~potentialities~~ features; namely the Auger systems and the XPS (X-rays ~~P~~ photoelectron ~~S~~ spectroscopy) systems.

[0003] Both ~~kinds~~ types of systems are based on detecting the kinetic energy of electrons emitted from the surface of the sample subjected to bombardment with electrons, or irradiation with X-rays.

The energies of the electrons emitted from the surface of the sample are characteristics of the elements and/or compounds present at the surface of the sample.

[0004] The Auger systems ~~permit to inspect~~

inspections to microareas of the sample surface down to a minimum linear dimension ~~in~~on the order of hundreds of ~~nm~~nanometers, and allows also a SEM (~~S~~secondary E~~electron M~~icroscope) visualization of the inspected area by scanning the area of acquisition of spectrometric data with the focused electron beam.

[0005] These systems have the drawback of permitting exclusively an elementary analysis. In other words, they are generally ~~incapable~~not capable of providing information on the chemical state of the identified elements because of the relatively weak chemical shift to which the Auger electron is subjected.

[0006] By In contrast, XPS systems offer the possibility of gathering information also on the chemical bonds besides those on the Auger electron. However, the XPS systems do not permit ~~to~~ restriction in the area of inspection beyond minimum linear dimensions ~~in~~on the order of hundreds of ~~nm~~micrometers because of the difficulty of focusing X-ray beams.

[0007] Because of this limitation, this technique is ~~hardly~~not suited to conduct inspections on microstructures, such as for example, the typical microstructures that are defined by modern fabrication processes of integrated circuits.

[0008] Moreover, XPS systems generally do not permit ~~to visualize~~visualization of the inspected area from which spectrometric data are acquired because the X-rays do not lend themselves to be used for scanning the

area. Visualization is possible, but at present the common approach remains that of using a dedicated auxiliary SEM column for visualizing the area through the secondary emitted electrons. However, this auxiliary visualization approach is not rigorously tied to the exciting X-ray beam directed ~~on to~~ onto the sample for the analysis, ~~being the exciting sources distinct.~~

[0009] It is evident ~~that~~ that there is a need and usefulness of a spectroscopic investigation system capable of yielding information also on the chemical state, ~~alike~~ like a XPS system, but which at the same time would allow one to carry out an investigation on a microspot, ~~that is.~~ The microspot may be on areas ~~of having~~ submicrometric linear dimensions, similarly to what is possible ~~to do~~ with the known Auger systems. ~~To this pressing need the present applicant has found an effective answer.~~

[0010] ~~It has been found that it is possible to~~ obtain reliable information on the chemical state, that is on the energy of the chemical bond of an element, by analyzing the kinetic energy distribution of electrons emitted from an irradiated sample, by causing emission of electrons by irradiating the microarea of interest with a substantially monoenergetic electron beam.

[0011] Notably, the chemical bond energy (BE) is given by the following relationship-:

$$BE = h\nu - KE - \Omega, (1)$$

where $h\nu$ is the energy of the incident particles or photons, KE is the kinetic energy of the emitted electrons, and Ω is the extraction energy.

Of course, the higher the resolution of the $h\nu$ term the more accurate will be the information on the chemical bond.

~~The present applicant has found that a~~

[0012] A beam of sufficiently energetic electrons that may be focused on a relatively small area of interest (microspot) of the surface of the sample, may be obtained by using a Field Emission Gauge (FEG) source of electrons and an appropriate energy filter (monochromator) capable of ensuring an energy resolution practically comparable to that of an X-ray monochromator.

[0013] Compared to the known systems using a focused electron beam such as the SEM, TEM, Auger and alike systems, all characterized in that they normally use thermo-ionic electron sources (hot sources), such as for example, a hot tungsten source or a hot LaB_6 source, there are others electron sources ideally suited to applications requiring a high spatial resolution. Field emission electron sources such as ~~the so-called~~ Schottky and "cold-cathode" sources have dimensions that generally are ~~comprised between~~ a few ~~nm, nanometers~~ in the case of a cold-cathode source, and about 15 ~~nm nanometers~~ in the case of Schottky sources. These dimensions are far smaller than those of the commonly use hot tungsten or LaB_6 sources that are ~~inon~~ the order of at least 10.000 nm, and normally much larger.

[0014] In addition, Schottky emission and cold cathode emission sources have the advantage of a much reduced energy dispersion of the emitted electrons, generally less than ~~1 eV~~ 1 eV, and a high brightness, that may be even several orders of magnitude greater than that of the hot cathode sources of LaB₆ or tungsten. Generally the brightness of Schottky or of cold cathode sources is greater than ~~10⁸ A/cm² SR~~ For the objectives.

Summary of the Invention

[0015] In view of the foregoing background, an object of the present invention, is to provide a spectroscopic system that yields information on the chemical state of a sample but at the same time allows an investigation to be conducted on a microspot.

[0016] A Schottky source is preferable compared to a cold cathode source because a Schottky source, besides the low energy dispersion characteristic and high brightness, is ~~far more easy~~ easier to use and has an outstanding short term stability of the electronic current of the beam, which is generally lower than 1% RMS.

[0017] ~~Moreover, for the objectives of this invention,~~ it is essential to employ an energy filter ~~offor~~ for the electron beam being focused on the surface of the sample under examination.

Energy filters are often called "monochromators", and their figure of merit is the smallest energy dispersion they are able to ensure in the filtered beam, such in order to convey on to onto the sample to be analyzed a

focused electron beam having substantially a planar wave front.

[0018] The are several known techniques for monochromatizing an electron beam ~~are several~~. Most commonly, the approach is that of applying a magnetic-electrostatic correction ~~of to~~ the trajectory of an electron traveling through a certain spatial region that may be semispherical (HEA, ~~"Hemispherical E - hemispherical energy Analyzer"~~) [1], or having a quadruple structure (Wien filter, possibly in cascade) [2], [3], known also as "mandolino" [4], or as typically implemented in transmission electron microscopes (TEM) for conducting ~~a~~-EELS (~~E~~electron ~~E~~energy ~~L~~oss ~~S~~spectroscopy) studies ("truncoidal monochromator TM") [5], wherein, always ~~by means of~~ electromagnetic lenses, electrons of a defined kinetic energy are gathered and exit the monochromator.

[0019] There are ~~innumerable~~ a number of monochromator filters for electron beams described in the literature. Basically, all these filters are based on the principle that electrons that do not possess the selected kinetic energy are electromagnetically deflected over different trajectories from the trajectory of electrons having the desired kinetic energy, which normally coincides with the central axis of the deflecting device. The deflected electrons are eventually suppressed by collecting them on a collector, or in some cases, electrons are re-focalized by guiding them along an appropriately designed path so that they emerge from the spatial sector relative to the desired kinetic energy value.

~~It has been found that the~~

[0020] The energy dispersion in the electron beam that may be obtained by employing such a monochromator filter for electron beams may be practically reduced to a fraction of eV₁ and that under such conditions₁ the ~~so~~ monochromatized electron beam is suitable to produce the required analytical results.

[0021] Even the level of electronic current that may be obtained through these monochromators, which normally may reach up to about ten nA, is satisfactory ~~for to meet the objectives~~ objective of the invention.

[0022] ~~The novel spectroscopic system of in~~ accordance with this invention ~~besides its not only has~~ the ability to determine the chemical bond existing among elements present on the microarea scanned by the monochromatic electron beam of excitation of the sample, but also ~~also to visualize~~ visualization of the scanned area in a way that is ~~perfectly~~ similar to what happens in a known Auger system, ~~which by.~~ In contrast, an Auger system is unable to provide information on the chemical state of the detected elements.

Brief Description of the Drawings

[0023] Figure 1 is a basic diagram of ~~the a~~ spectroscopic analysis system ~~of in~~ accordance with this invention.

[0024] Figures 2, 3 and 4 are spectrograms obtained from preliminary tests that demonstrate the effectiveness of the ~~novel method of this invention.~~

method in accordance with the invention.

Detailed Description of the Preferred Embodiments

[0025] Figure 1 is a basic diagram of an electron spectroscope implementing this invention.

The field emission electron source is preferably a Schottky emission source, ~~f.~~ For example it, the field emission electron source may be of the type produced by the company FEI of the Philips group or by the Japanese company Denka.

[0026] The monochromator energy filter of the focused electron beam may be any commercially available filter capable of ensuring a maximum energy dispersion of the electrons of the beam exciting the filter of less than 0.2 eV, and more preferably less than 0.1 eV.

[0027] ~~The so~~ filtered electron beam is directed on the surface of the sample ~~to being~~ analyzed. The irradiated area may have linear dimensions as small as ~~in the order 100 nm and, or~~ even less.

Of course, scanning ~~of~~ a certain area of the sample is done as in any other known focused electron beam system.

~~The a~~ Analysis of the kinetic energy spectrum of the electrons emitted from the excited area of the sample is carried out with a common spherical capacitor energy analyzer.

[0028] Decelerating and focusing ~~means~~ of electrons emitted from the excited area of the sample ~~for producing~~ produce a spectrum representatives of the

distribution of the kinetic energies of the emitted electrons over an inlet aperture of ~~said~~the energy analyzer, ~~a.~~ A detector ~~for detecting~~detects the electrons traveling through the energy analyzer for reproducing the distribution of the kinetic energies of the emitted electrons along at least a direction orthogonal to the radial direction of said spherical capacitor of the analyzer.

[0029] Preliminary tests have been conducted on SiO₂ and Ti samples and the results as shown in Figures 2, 3 and 4.

~~The validity~~

[0030] Validity of the ~~novel~~ approach of the ~~applicant was~~disclosed herein has been demonstrated by a number of laboratory tests that have been carried out using the available commercial micro Auger system of Physical Electronics, Model 670, notwithstanding that, as with the normally available systems of this type, ~~it~~ was equipped with a common electron source of ZrO₂ coated tungsten. The machine had ~~and a~~ CMA (~~C~~ylindrical M~~m~~irror A~~a~~nalyzer) detector, coaxial to the incident electron beam. That is ~~a~~ proof of the validity ~~of the novel technique~~that was sought notwithstanding that a recognizably more effective apparatus using an electron source of reduced energy dispersion was not available.

[0031] Different electron accelerating voltages were used, respectively ~~of~~ 3.5 and 3.0 kV, with electronic current of about 10nA, in order to place ~~in evidence~~ the shift of the detected ~~peak~~peak upon the varying of the accelerating voltage, ~~in order~~and to demonstrate the

dependence of the position of the peak in the spectrum from the accelerating voltage of the exciting beam.

[0032] For a first test ~~a sample of,~~ an ultra pure SiO₂ sample of 100 nm of thickness, produced by thermo deposition on silicon ~~has been~~ was used and the sample ~~has~~ had been analyzed without any prior cleaning of the surface, neither by chemical cleaning solutions or ion bombardment.

[0033] By observing the obtained spectrogram reproduced in Figure 2, it may be noted that with an electron beam accelerated at 3.5 kV, a peak appears at 2,970 eV which, from the relationship (1), which yields a BE of 530 eV.

[0034] The precise value of the extraction energy (Ω) term should eventually be determined experimentally using appropriate calibration samples. For the purposes of these preliminary tests, the value attributed to it was considered to be a first approximation, missing an absolutely precise value of the term Ω (determined by specific tests) to be used in equation (1), ~~n.~~ Nevertheless, the result appeared to be very close to the known BE of the oxygen core level 1s, which in SiO₂ is reported in the literature to be ~~of~~ about 533-534 eV. [6].

[0035] As commonly done in an Auger system, the spectrum was numerically differentiated in order to give more emphasis to the ~~neighborhood~~ neighborhood of the detected peak.

~~In order to~~ To further demonstrate the validity of the

~~novel~~ approach disclosed herein, a different sample of ultra pure titanium deposited on SiO_2 hasd been used. The sample showed the presence of a superficial film of native titanium oxide.

[0036] The spectroscopic analysis was carried out under the same experimental conditions of the preceding test, that is, at the same accelerating voltage and electronic current, using the same commercially available apparatus, without any cleaning of the sample surface.

The obtained spectrogram is reproduced in Figure 3. It may be noted that, with an accelerating voltage of 3.5 kV, a definite peak appears at 3,054 eV, which from the relationship (1), using a first approximation value for the term Ω , yields a BE of 446 eV.

[0037] Even in this case the exact value of the term Ω was not determined, ~~t.~~ Therefore, the attributed value of BE is just a first approximation estimate that comfortably compares with the value of Ti Core 2p $3/2$, ~~that i.~~ In literature, it is indicated as being equal to 453-454 eV [6].

Even in this case, a numerical differentiation of the spectrum has been introduced for better detailing the zone of interest.

[0038] Finally, it has been proved that the ~~novel~~ test model in accordance with the invention remains valid not just among different materials but also upon the varying of the accelerating voltage of the exciting electrons. For this purpose, the same Ti sample used in the preceding test has been used ~~lowering to lower~~ lowering to lower the

acceleration in voltage from 3.5 to 3.0 kV.

[0039] ~~If the test model of this invention is valid,~~
~~then~~ the expectation is that ~~also~~ the peak also shifts
 by a difference equal to the energy difference of the
 exciting electron beam.

[0040] As may be clearly observed in Figure 4, the
 result of this further test has been that of an
 estimated BE of 451 eV, to be compared with the value
453-454 eV reported in the literature ~~453-454 eV~~ [6].
 Compared to the preceding test, a change of about 5 eV
 in the estimated value of the BE is observed (in the
 preceding test the BE was found to be 446 eV), at the
 changed accelerating voltage. However, it is to be
 considered that by decreasing the accelerating voltage
 the probability of ionizing the substrate decreases,
 thus implying a lowering of the intensity of the
 detected signal together with a dispersion thereof.
 Moreover, it is also possible that by varying the
 accelerating voltage by 500 eV, the Ω function, may
 itself vary, ~~being since~~ this parameter is dependent on
 the system ~~in its whole~~.

~~Notwithstanding the fact that,~~

[0041] Even though the tests have been carried out
 using a commercially available apparatus (an Auger
 system employing a hot cathode electron source)
~~therefore that is~~ not optimized for the novel test
 approach ~~of~~ in accordance with this invention, and from
 these tests it may ~~be~~ reasonably be deduced that the
 substrate, whichever it is, has reacted to the external
 electron excitation by emitting a signal (emitted
 electrons) that appears to carry information on the

superficial chemical state of the detected elements, thus proving the validity of the inventors assumption test approach.

[0042] Due to these relative ~~rudimentaryness~~ fundamentals of the tests, it has not been ~~impossible~~ possible to obtain ~~signals of~~ relatively large ~~managed to be~~ signals confirmed with a higher precision as aligned with the expected data from the literature, ~~h.~~ However, with the ~~evident~~ good approximation of the estimate ~~such as~~ obtained with the ~~rudimental~~ basic (not fully optimized) apparatuses ~~in the case at upon an appropriate design phase, the novel technique of~~ in accordance with this invention will usefully inscribed itself among the known techniques (Auger, EELS and XPS), ~~characterizing itself.~~ The technique will be characterized as being able to produce useful information on the chemical state of the detected elements without the limitations of the size of the inspected area of comparable known systems.

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~~C-L~~ ~~AT~~ THAT WHICH I-M-SS CLAIMED IS:

1. An electroscope system based on exciting a certain area of the surface of a sample to emit electrons with a characteristic distribution of kinetic energies, comprising a spherical capacitor energy analyzer, decelerating and focusing means of electrons emitted from the excited area of the sample for producing a spectrum representatives of the distribution of the kinetic energies of the emitted electrons over an inlet aperture of said energy analyzer, a detector for detecting the electrons traveling through the energy analyzer for reproducing the distribution of the kinetic energies of the emitted electrons along at least a direction orthogonal to the radial direction of said spherical capacitor of the analyzer, characterized in that the area of said sample is excited by an electron beam produced by a filed emission source and by a monochromator energy filter of said electron beam disposed long stream of said electron source.

2. The spectroscopy system according to claim 1, wherein said monochromator energy filter reduces energy dispersion of the electrons of said electron beam to less than 0.2 eV.

**ELECTRON SPECTROSCOPE WITH EMISSION INDUCED BY A
MONOCHROMATIC ELECTRON BEAM**

~~A B S T R A C T~~

Abstract of the Disclosure

An electroscope system ~~based on~~
~~exciting~~excites a certain area of ~~the~~a surface of a
sample to emit electrons with a characteristic
distribution of kinetic energies, ~~has t.~~The analyzed
area of the sample is excited by an electron beam
produced by a field emission source ~~and a.~~A
monochromator energy filter ~~of said~~for the electron
beam ~~disposed~~is down-stream of the ~~electron~~field
emission source.

The field emission electron source is preferably a
Schottky source, and a monochromator energy filter
reduces energy dispersion of the electrons of ~~said~~the
electron beam to less than 0.2 eV.

Microareas of linear dimensions ~~in on~~in the order of ten
~~nm~~nanometers may be analyzed while observing them,
~~gathering i.~~Information on the chemical state of the
detected elements present at the surface of the
examined microarea of the sample is gathered.